Investigations in organotitanium chemistry

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CHAPTER 2.

KINETICS OF THE CO INDUCED DISPROPORTIONATION OF $(\eta^5\text{-}C_5Me_5)_2TiCl$.

Summary

The disproportionation of $Cp^*_2Ti(Cl)CO$, formed in *situ* from Cp^*_2TiCl and CO in toluene solution, to $Cp^*_2TiCl_2$ and $Cp^*_2Ti(CO)_2$ has been studied at CO pressures between 2 and 90 bar. The reaction rate was found to be inversely proportional to the CO concentration. The reaction order with respect to $Cp^*_2Ti(Cl)CO$ changed from 1 to 1.4 with increasing CO pressure. These observations are explained in terms of a kinetic scheme in which Cp^*_2TiCl, which is reformed from $Cp^*_2Ti(Cl)CO$ in a slow reaction, is an essential intermediate.

Introduction

The CO–induced disproportionation of $(Cp_2TiCl)_2$ to $Cp_2Ti(CO)_2$ (Cp: η^5–C_5H_5) was reported[1'] to proceed by a reaction between monomeric Cp_2TiCl and its CO adduct $Cp_2Ti(Cl)CO$. In the rate–determining step the latter appears to transfer its chlorine ligand to the uncomplexed monomer to give Cp_2TiCO, which in the final step complexes another molecule of CO. The object of the present study is to elucidate the kinetics and mechanism for the CO–induced disproportionation of the closely related complex Cp^*_2TiCl (Cp*: η^5–$C_5(CH_3)_5$)[19] and to determine in which way differences in electronic and steric properties of the permethyl substituted ring affect disproportionation and comproportionation reactions.[20]

Experimental

All operations were performed under rigorous exclusion of oxygen and moisture using standard vacuum–line techniques. Solvents were distilled from sodium metal, carefully degassed and saturated with argon prior to use. Gases (ultrahigh purity) were used as purchased. Cp^*_2TiCl **(1)** and $Cp^*_2Ti(CO)_2$ (2) were prepared by published procedures.[21] NMR experiments were performed in benzene–d, under CO (ca 750 torr) in sealed NMR tubes. For IR measurements under elevated pressure a pressure–resistent IR cell was used as previously

described[1] (Figure 1). Kinetic measurements were carried out with 0.05 M solutions of Cp^*_2TiX in toluene. IR absorbance data were collected and processed as before.[1] Kinetic runs were reproducible to within 10%. Concentrations of $Cp^*_2Ti(Cl)CO$ (**4**) and $Cp^*_2Ti(CO)_2$ (**2**) were monitored in time at their respective absorption maxima (2014 cm^{-1} for **4** (ε = 350 (30) $L.cm^{-1}.mol^{-1}$) and 1849 cm^{-1} for **2** (ε = 1020 (50) $L.mol^{-1}.cm^{-1}$)).

Figure 1. Pressure resistent IR–cell.

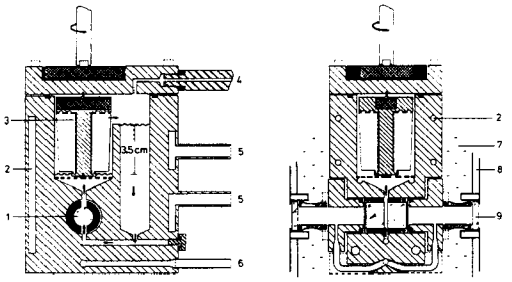

Fig. 1. Pressure-resistant IR cell with internal, isobaric and isothermal circulation. Essential parts: 1, inner, pressure-resistant CaF_2 windows (13 mm thick, 18 mm diam.); 2, channels for thermostatted heat-transfer liquid; 3, internal centrifugal rotor, driven by rotating external magnet bar; 4, inlet/outlet for sample solutions and gases; 5, inlet/outlet for heat transfer liquid; 6, evacuation of space between inner and outer CaF_2 windows; 7, removable foam-rubber insulation; 8, polyvinyl casing; 9, outer CaF_2 windows. Direction of circulation of the sample solution between rotor-agitated gas-liquid mixing chamber, solution reservoir and IR window gap as indicated by small arrows.

Results

Characterization of Reaction Products and Intermediates.

When **1** is treated with CO, disproportionation to $Cp^*_2TiCl_2$ (**3**) and $Cp^*_2Ti(CO)_2$ (**2**) (eq 1) is observed[2]; this reaction is fast at room temperature and CO pressures of or above 1 bar. In contrast to the analogous reaction with $(Cp_2TiCl)_2$, the disproportionation is irreversible[2]: Removal of the CO atmosphere does not lead to the disappearance of the ^1H NMR signals of **2** and **3** by comproportionation to **1**. Also no reaction was observed between **2** and **3** when mixed together in toluene.

$$\underset{\mathbf{1}}{2\ Cp^*_2TiCl} + 2\ CO \longrightarrow \underset{\mathbf{3}}{Cp^*_2TiCl_2} + \underset{\mathbf{2}}{Cp^*_2Ti(CO)_2} \qquad (1)$$

IR spectroscopic studies of the carbonylation of the monohalide **1** was performed as described by Van Raaij et al. for the related $(Cp_2TiCl)_2$ (cf. Figure 1)[1]. Reaction of **1** with CO at low temperature (*e.g.* –30 °C) and pressures higher than 2 bar gives only evidence for the formation of the monc carbonyl adduct $Cp^*_2Ti(Cl)CO$ (**4**). Its formation is quantitative within the

time needed to saturate the solution (ca 3 min) and its concentration is independent of CO pressure between 2 and 90 bar. This means equilibrium 2 lies fully to the right hand side. This is in contrast with $(Cp_2TiCl)_2$ where formation of the $Cp_2Ti(Cl)CO$ adduct is quantitative only at pressures well over 100 bar. Both the higher electron density at the metal centre[3] and the monomeric nature of Cp^*_2TiCl are likely to contribute to the enhanced stability of $Cp^*_2Ti(Cl)CO$ compared to $Cp_2Ti(Cl)CO$.

$$\underset{\mathbf{1}}{Cp^*_2TiCl} + CO \rightleftharpoons \underset{\mathbf{4}}{Cp^*_2Ti(Cl)CO} \qquad (2)$$

Compound **4** is stable at –30 °C and shows no tendency either to disproportionate to **2** and **3** (eq 1) or to lose CO and form **1**. Even when the CO pressure is released and residual CO is swept from the solution with nitrogen gas no decrease in the concentration of **4** is observed. At –10 °C, **4** is also formed quantitatively, and appears to be stable under CO. However, when the CO atmosphere is replaced by nitrogen, a slow decrease of the amount of [**4**] (half–life time ca 14 h) is observed. After ca 30% of the original amount of **4** has disappeared, characteristic ν_{CO} absorptions of $Cp^*_2Ti(CO)_2$ (**2**) appear and indicate the beginning of a disproportionation of **4** into **2** and **3**. At higher temperatures (> 0 °C) the changes in concentration of **4** and **2** can be measured conveniently and kinetic studies are possible.

The facile disproportionation of **1** with CO prompted us to study whether similar reactions can be induced by other substrates, such as ethene, since the stable titanium(II) species $Cp^*_2Ti(\eta^2\text{–}C_2H_4)$ is well characterized.[22] However, the characteristic IR–absorption of this complex at ν = 3655 cm^{-1} was not observed at any ethene pressure up to 40 bar. Equally negative results were obtained with respect to the conceivable reaction of **1** with hydrogen (90 bar) to **3** and $Cp^*_2TiH_2$[23] or to Cp^*_2TiHCl[24].

Kinetic Analysis of the CO Induced Disproportionation of Cp^*_2TiCl (1).

At 5 °C and pressures above 10 bar, complete conversion of **1** into **4** is initially observed. At this temperature the disproportionation reaction appears to be substantially slower than the formation of **4**, so that **4** builds up to a maximum concentration, which is practically equal to the initial concentration of **1** (Figure 2).

Figure 2. Disproportionation of $Cp^*_2Ti(Cl)CO$ (**4**) to $Cp^*_2Ti(CO)_2$ (**2**) and $Cp^*_2TiCl_2$ (**3**) at 5 °C under CO pressures from 10 to 90 bar. A: **4** monitored, B: **2** monitored.

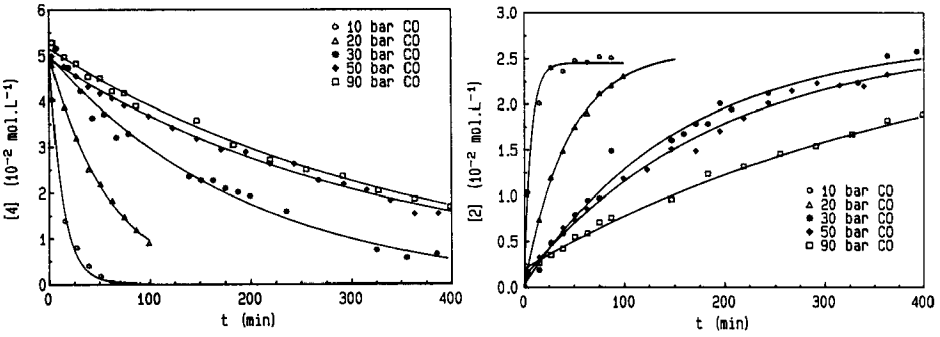

Table 1. Apparent rate constant k_{obs} in dependence of CO pressure at 5 °C (from ln $([4]_t/[4]_0) = k^{decr}_{obs}.t$ and $\ln(1 - [2]_t/[2]_\infty) = k^{incr}_{obs}.t$)

P_{CO} (bar)	k^{decr}_{obs} (min^{-1})	k^{incr}_{obs} (min^{-1})	order in [4]
10	0.066 (7)	0.068 (7)	1.0
20	0.0094 (9)	0.012 (10)	1.3
30	0.0064 (6)	0.0064 (6)	1.3
50	0.0043 (4)	0.0046 (4)	1.3
70	0.0031 (3)	0.0032 (3)	1.4
90	0.0023 (3)	0.0024 (3)	1.4

The rate of the subsequent conversion of **4** into **2** and **3** depends on the CO pressure (Table 1). Remarkably, the observed rate constant is inversely proportional to CO concentration (Figure 3). This contrasts the observations for the analogous reaction of $(Cp_2TiCl)_2$, which is accelerated by increase in the CO pressure. The decay of **4** and the concomitant increase in the amount of **2** is close to first order with respect to **4**. The overall order in [**4**] depends on the CO concentration; it increases from n = 1 to 1.4 as the CO pressure is increased from 10 to 90 bar. This was established by analyzing the kinetic data by several methods[25] and independently by using various initial concentrations of **1**: At 70 bar CO pressure, for instance, the first half-life changed from $\tau_{1/2}$ = 170 min for [**4**] = 0.05 mol.L^{-1} to $\tau_{1/2}$ = 220 min for [**4**] =

0.025 mol.L^{-1}, thus indicating a reaction order of n = 1.4 in **4** over that concentration interval.

Figure 3. Inverse of observed rate constant k_{obs} vs CO concentration at 5°C.

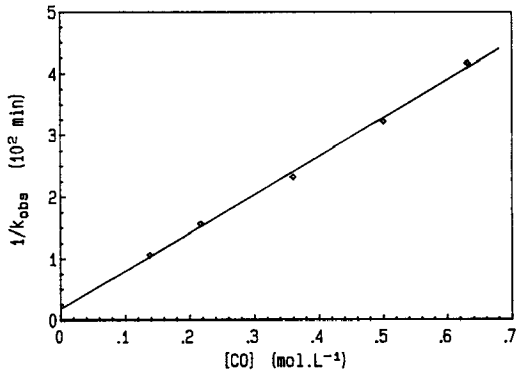

Table 2. Apparent rate constant k_{obs} in dependence of CO pressure at 12 °C (k_{obs}^{decr}, k_{obs}^{incr} cf. Table 1).

P_{CO} (bar)	k_{obs}^{decr} (min^{-1})	k_{obs}^{incr} (min^{-1})
10	0.10 (2)	–
20	0.018 (2)	0.019 (2)
30	0.013 (2)	0.012 (2)
50	–	0.007 (1)

At still higher temperatures (12 °C) the initial formation of **4** is no longer quantitative, some **2** (up to 40%) already being formed in the time necessary to saturate the solution with CO. At this temperature the disproportionation rate is comparable to that of formation of **4**. Higher CO pressures retard the former process to some extent, probably due to the faster decrease of **1**. After the fast initial reaction during the first few minutes, a much slower disproportionation is observed to follow the rate law in eq 3 (Table 2).

$$v = -\frac{d[\mathbf{6}]}{2dt} = \frac{d[\mathbf{2}]}{dt} = k_{obs}[Ti]^{1-1.4} \qquad (3)$$

At 50 bar CO pressure the temperature dependence of k_{obs} gives a linear Eyring plot with $\Delta H^{\ddagger}$ = 80 (12) kJ.mol^{-1} and $\Delta S^{\ddagger}$ = 105 (30) J.mol^{-1}.K^{-1} (Table 3).

Table 3. Apparent rate constant k_{obs} in dependence of temperature at 50 bar CO. (k_{obs}^{decr}, k_{obs}^{incr} cf. Table 1).

T (°C)	k_{obs}^{decr} (min^{-1})	k_{obs}^{incr} (min^{-1})
12	–	0.007
5	0.0043	0.0046
0	0.0013	0.0013
−5	0.00072	0.00082

Discussion and Conclusions

The observations reported above can be explained by Scheme 1, which is comparable to that relevant to the CO induced disproportionation of $(Cp_2TiCl)_2$.

$$\underset{\mathbf{4}}{Cp^*_2Ti(Cl)CO} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} \underset{\mathbf{1}}{Cp^*_2TiCl} + CO \qquad (4)$$

$$\underset{\mathbf{4}}{Cp^*_2Ti(Cl)CO} + \underset{\mathbf{1}}{Cp^*_2TiCl} \xrightarrow{k_{ir}} \underset{\mathbf{3}}{Cp^*_2TiCl_2} + \underset{\mathbf{5}}{Cp^*_2TiCO} \qquad (5)$$

$$\underset{\mathbf{5}}{Cp^*_2TiCO} + CO \xrightarrow{fast} \underset{\mathbf{2}}{Cp^*_2Ti(CO)_2} \qquad (6)$$

SCHEME 1

The decrease in the reaction rates at higher CO pressures results from the inverse dependence of the steady state concentration of **1** on CO concentration. The observation that the reaction becomes higher than first order in **4** at higher CO pressures suggests that **1**, which is slowly formed from **4**, reacts with CO and with **4** at comparable rates: If $k_f \cdot [CO] \ll k_{ir} \cdot [\mathbf{4}]$ the overall reaction order, n, would be 1, whereas if $k_f \cdot [CO] \gg k_{ir} \cdot [\mathbf{4}]$ then the reaction order would be 2.[26] A steady state approximation for the concentration of **1** (a reaction intermediate of low and approximately constant concentration) results in the rate expression in eq 7.

$$-\frac{d[4]}{2dt} = \frac{d[2]}{dt} = \frac{k_d\ k_{ir}\ [4]^2}{k_f[CO] + k_{ir}[4]} \qquad (7)$$

Integration of eq 7 leads to an expression containing both inverse and logarithmic terms in the concentration of **4**. Accordingly, the overall order in [**4**] will indeed be somewhere between 1 (logarithmic in [**4**]) and 2 (inverse in [**4**]). Instead of numerically evaluating the individual rate constants from the experimental curves, we propose to use the approximation given in eq 8, which is valid at least for the first half-life within an error of 10% (See Appendix)[27], and allows the determination of k_{obs} from the slope of a plot of ln [**4**] against time.

$$[4]_t = [4]_0 \exp(-k_{obs}.t), \text{ with} \qquad (8)$$

$$1/k_{obs} = \tfrac{1}{2}\ k_d\ (1 + [CO].k_f/([4]_0.k_{ir})) \qquad (9)$$

By plotting $1/k_{obs}$ against the CO concentration (eq 9) we determined k_d and the ratio of k_f/k_{ir} (neither of these two rate constants can be measured independently). At 5 °C we find k_d = 0.029 (10) min^{-1} and k_f/k_{ir} = 1.8 (2). The dissociation of CO from **4** can thus be regarded as the rate-limiting step for the disproportionation reaction. At low CO pressure the observed rate constant k_{obs} is practically equal to k_d; at higher CO pressures the reverse reaction of **1** with CO becomes increasingly competitive with the irreversible disproportionation, in accord with eq 5. The ratio $[CO].k_f/([4].k_{ir})$ which increases from ca 2.3 at 10 bar to 23 at 90 bar, indicates that back reaction to **4** is indeed fastest, especially at higher CO pressures. Scheme 1 also explains the fast initial reaction phase at low CO pressures and higher temperatures (12 °C): During the saturation of the solution with CO, **4** is formed in the presence of comparable amounts of unreacted **1**, so that their mutual reaction (eq 5) is not held up by the need to dissociate CO from **4**. As the concentration of CO increases and that of **1** is depleted, the system approaches the steady-state condition discussed above.

The activation parameters observed for the reaction 2 $Cp^*_2Ti(Cl)CO \longrightarrow Cp^*_2Ti(CO)_2 + Cp^*_2TiCl_2$, $\Delta H^{\ddagger}$ = 80 (12) kJ.mol^{-1} and $\Delta S^{\ddagger}$ = 105 (30) J.mol^{-1}.K^{-1}, are in accordance with the proposal that dissociation of CO from $Cp^*_2Ti(Cl)CO$ is rate-limiting: Comparable values of $\Delta H^{\ddagger}$ (100 – 120 kJ.mol^{-1}) and $\Delta S^{\ddagger}$ (49 – 63 J.mol^{-1}.K^{-1}) have been reported by Basolo and coworkers[28] for ligand exchange reactions of $Cp_2Ti(CO)_2$ and $Cp^*_2Ti(CO)_2$, which have a dissociative mechanism.

As proposed for the analogous reaction with $(Cp_2TiCl)_2$, the disproportionation of $Cp^*_2Ti(Cl)CO$ to $Cp^*_2Ti(CO)_2$ and $Cp^*_2TiCl_2$ appears to involve a transfer of a Cl ligand from $Cp^*_2Ti(Cl)CO$ to Cp^*_2TiCl. It indicates that despite the very bulky Cp* ligands no insuperable steric constraints exist for two permethyl titanocene units to react with each other. The differences between Cp^*_2TiCl and $(Cp_2TiCl)_2$ with respect to their reactions with CO result from the greatly different stabilities of their respective monocarbonyl adducts: At CO pressures below 100 bar, the reaction rate for $(Cp_2TiCl)_2$ increases linearly with CO pressure and only begins to level off at about 130–140 bar. An inverse dependence of the disproportionation rate on the CO concentrations, as observed for $Cp^*_2Ti(Cl)CO$ would be expected for $(Cp_2TiCl)_2$ only at CO pressures far exceeding the experimentally possible range. The kinetics of the reaction of Cp^*_2TiCl with CO can thus be regarded as corresponding to those of $(Cp_2TiCl)_2$ at the very high pressure limit.

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9. CO concentrations were calculated from P(CO) by the relationship $[CO] = P(CO).(7.1 \cdot 10^{-3}) - (P(CO))^3.(2.2 - \delta.9 \cdot 10^{-2}).10^{-8}$ (δ : temp in °C).[1b]
10. In fact the agreement with (eq 8) was found to be quite good for a period of over two half–lifes.
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Appendix

Scheme 1 can be represented by the following equations (A1,A2):
(A : [4], B: [1], D: [2], E: [3])

$$A \underset{k_f}{\overset{k_d}{\rightleftharpoons}} B + CO \qquad (A1)$$

$$A + B \xrightarrow{k_{ir}} D + E \qquad (A2)$$

$$-\frac{dA}{dt} = k_d A - k_f[CO]B + k_{ir}AB,$$

$$-\frac{dB}{dt} = -k_d A + k_f[CO]B + k_{ir}AB$$

$$-\frac{dD}{dt} = -k_{ir}AB$$

Steady–state approximation ($\frac{dB}{dt} = 0$) yields $B = \frac{k_d A}{k_f[CO] + k_{ir}A}$ and

$$-\frac{dA}{2dt} = \frac{k_{ir}k_d A^2}{k_f[CO] + k_{ir}A} = \frac{dD}{dt} \qquad (A4)$$

The integrated form ($A_r = A_t/A_0$),

$$\left(-\frac{k_f[CO]}{2k_{ir}k_d A_0}\ \frac{1}{A_r} + \frac{1}{2k_d}\ln(A_r A_0)\right)\Big|_1^{A_r} = -t \qquad (A5)$$

can be approximated for $A_r < 0.5$ within an error limit of 10% by A6:

$$\left(-\frac{k_f[CO]}{2k_{ir}k_d A_0}(1 - \ln A_r) + \frac{1}{2k_d}\ln(A_r A_0)\right)\Big|_1^{A_r} = -t \qquad (A6)$$

leading to : $\ln(A_t/A_0) = -\frac{2k_d k_{ir}A_0}{k_{ir}A_0 + k_f[CO]} \cdot t$ (A7)